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**CRYOGENIC LASER CALORIMETRY  
FOR IMPURITY ANALYSIS**

**FINAL REPORT**

**Period of Performance 9/6/83 to 12/1/84**

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#### **NEW TECHNOLOGY**

**No new technology is reportable for the period covered by this report.**

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## ABSTRACT

This report presents the results of a one-year effort to determine the applicability of laser-calorimetric spectroscopy to the study of deep-level impurities in silicon. Critical considerations for impurity analysis by laser-calorimetric spectroscopy are discussed, the design and performance of a cryogenic laser calorimeter is described, and measurements of background absorption in high-purity silicon are presented.

## Introduction

This report presents the results of a one-year effort to determine the applicability of laser-calorimetric spectroscopy [1] to the study of deep-level impurities in silicon. There were three parts to the effort: to investigate the critical considerations in the application of calorimetric methods to deep level spectroscopy, to design and build a cryogenic calorimeter for spectroscopic measurements, and to carry out calorimetric measurements of optical absorption in silicon. All three stages of the effort were completed.

## Laser Calorimetric Spectroscopy

The goal in the application of calorimetric spectroscopy to the study of deep-level impurities is to develop an accurate method of measuring the impurity level energies using optical absorption methods. The reason for developing a cryogenic capability is to allow temperature-dependent studies of deep-level energies. The level energies are determined by measuring the photoabsorption cross section  $\sigma^0$  as a function of wavelength, and then fitting the data using a line-shape model.

The experimental configuration is shown in figures 1 and 2. Light from a laser illuminates the sample. The sample is mounted on the cryostat coldfinger, to which it is weakly coupled thermally. The sample temperature is monitored by a differential thermocouple, and temperature changes are detected by a nanovoltmeter, and recorded by a chart recorder.

Figure 3 shows a plot of typical data obtained by this method. The slope of the heating curve provides the principal



information on the absorbed power, and the slope of the cooling curve provides a correction for heat loss from the sample to its surroundings. The process is described by the equation:

$$P_{abs} = mc \left. \frac{dT}{dt} \right|_H - \left. \frac{dT}{dt} \right|_C$$

where  $P_{abs}$  is the absorbed power,  $m$  is the sample mass,  $c$  is the specific heat, and  $\frac{dT}{dt}$  is the temperature slope during heating and cooling, measured at the same temperature. From a knowledge of the absorbed power, the absorption coefficient  $\alpha$  is determined from the equation for the relative absorption (for  $\alpha l \ll 1$ ):

$$\frac{P_{abs}}{P_0} = \frac{(1-R)^2 \alpha l}{1-R^2(1-2\alpha l)}$$

Where  $R$  = single-surface power reflectivity,  $l$  = sample thickness, and  $P_0$  = incident power. The relationship of the absorption coefficient  $\alpha$  to the photoionization or photoneutralization cross section  $\sigma^o$  of a given deep-level transition depends on whether the absorption is primarily due to the deep level impurity, or to other absorption mechanisms. If deep-level absorption dominates, and if there is only one active deep-level transition, then the relationship is:

$$\alpha = N \sigma^o$$

where  $N$  is the number density of optically active deep impurities.

### Critical Considerations

The calorimetric method has been used in the past at this laboratory to measure relative absorptions as small as  $10^{-5}$  (i.e. 10 ppm).

Successful measurements of such small signals requires attention to details not evident in looking at the simple analysis equations. The primary means available for detecting systematic errors are by examining the heating/cooling curves for proper exponential behavior.

The limiting systematic error in laser calorimetry is usually heat leaks caused by stray light (scattered or reflected). A small amount of scattered light that is strongly absorbed by an apparatus component can result in erroneous signals greater than the true signal. For example, we have observed cases in which thin-foil light baffles have been heated by scattered light sufficiently to reradiate significant levels of power in the mid and far infrared at wavelengths for which the sample was strongly absorbing, resulting in order-of-magnitude errors. Additional errors occur if scattered light strikes the thermocouple. These problems are compounded by the confined space of a cryogenic calorimeter because of the difficulties of installing light baffles to control scattered light. Furthermore, the high reflectivity of silicon enhances multiple reflections. Careful alignment of the sample to be parallel to the cryostat windows, and normal to the laser beam is essential.

The major sample consideration for successful optical absorption spectroscopy of deep-level impurities is that deep-impurity absorption dominate all other absorption mechanisms. Possible sources of background absorption include free carrier absorption, absorption by precipitates and inclusions, two-photon band-to-band absorption (pulsed sources only), and

multiple-phonon indirect band-to-band absorption. The requirement of low free-carrier absorption is of special importance in the case of solar-cell grade silicon since such material is of relatively low resistivity. Consequently, solar cell material would have to be heavily doped with deep-level impurities in order for the deep-level signal to exceed the free-carrier signal. Fundamental studies of deep-level impurities are restricted to high-resistivity silicon.

For samples in which the deep-level absorption dominates, the level energy is determined by measuring the photoabsorption cross section as a function of incident photon energy. A typical photoabsorption cross section is shown in figure 4. The level energy is near but not at the measured threshold energy. The level energy cannot be accurately determined merely by measuring the upper part of the shoulder; it is necessary to follow the curve down as low as possible in the steep region near the threshold. Consequently, samples should be heavily doped with deep-level impurities in order that as much as possible of the impurity absorption signal lie above the background absorption signal due to other absorption mechanisms.

The reason that the photo cross section must be measured down as low as possible in the steep region near the threshold is that the line shape is strongly influenced by coupling to the lattice. The apparent level energy is therefore a combination of electronic and vibrational energies. The theory describing this coupling is not fully developed, although the configuration coordinate model and Huang-Rhys theory provide a beginning.

The coupling to the lattice has an additional effect i.e.: temperature dependence of the level energy. As shown by Van Vechten and Thurmond [2], the energies measured by optical absorption are Gibbs free energy changes  $\Delta G$ , whereas the energies measured by thermal activation are enthalpy changes  $\Delta H$ . These energies are not usually equal. Measurements of  $\Delta G$  and  $\Delta H$  may be reconciled by measuring the temperature dependence of  $\Delta G$ . The temperature derivative of  $\Delta G$  then provides the entropy change  $\Delta S$  of the deep level transition. The Gibbs free energy, the enthalpy, and the entropy are related by the equation

$$\Delta G = \Delta H - T\Delta S .$$

Additional useful information is contained in the entropy change  $\Delta S$ . This may provide clues as to the nature of the deep level defect.

#### Cryogenic Calorimeter Development

The calorimeter was designed using a Sulfrain liquid helium dewar, which for this work was operated using liquid nitrogen. The sample was suspended on thin nylon threads from posts that are an integral part of the dewar cold finger. A radiation shield with two 5mm diameter ports was mounted on the cold finger. The radiation shield was designed to accept quartz windows to block room-temperature radiation at wavelengths beyond  $3 \mu\text{m}$ , but this refinement proved to be unnecessary. Since the sample is only weakly coupled thermally to the cold finger, its steady state temperature was strongly influenced by the radiation shield. It was found that for liquid nitrogen operation (77K),

the steady state sample temperature was 90K with the radiation shield in place, and 180K without the radiation shield.

Sample temperature was measured using a differential thermocouple of 3-mil diameter copper-constantan wire. The thermocouple reference junction was glued to the cold finger, and the sample junction was glued to the sample using a very small quantity of GE7031 varnish. This was heat-cured using a soldering iron, and using the thermocouple to monitor the varnish temperature. It is important that the smallest-possible amount of varnish be used in order to avoid a false signal due to absorption of scattered light by the varnish during spectroscopic measurements.

As a preliminary test of signal calibration, the calorimeter was operated as a power meter. This was done by illuminating a silicon sample with red light (6328 Å) from a HeNe laser. At this wavelength, all light that was not reflected was absorbed. Therefore, the rate of temperature change could be predicted, knowing the incident power. Comparison of the calculated and measured rates of temperature change showed that the measured rate was about 40% lower than predicted. This discrepancy is presumably due primarily to errors in the assumed heat capacity. Two effects are responsible for this discrepancy. The first is that the contribution of free carriers to the heat capacity was not included. This is known to be a significant effect. The second is that the sample was thermally coupled to the cold finger, and so some prorated contribution to the heat capacity due to this coupling must be included. Therefore, in order to

directly measure the heat capacity by electrical heating, an insulated constantan wire was wrapped around the sample. While this method avoids the problem of assuming a heat capacity, it introduces an additional risk of a false signal due to absorption of scattered light by the heater wire during spectroscopic measurements. Therefore, the preferred method is to calibrate the heat capacity electrically, and then remove the wire for the spectroscopic measurement, correcting for the heat capacity of the absent heater wire.

### Spectroscopic Measurements

In order to determine the residual background absorption, the ultimate limiting factor in deep level optical absorption spectroscopy, absorption measurements were carried out in high resistivity silicon at two wavelengths. The sample was float-zone silicon purchased from Wacker Siltronic. It had a resistivity of  $10^4$   $\Omega$ -cm, and a free-carrier lifetime of  $5 \times 10^{-3}$  s. The measurements were carried out at room temperature.

The first measurement was carried out at a wavelength of  $1.9 \mu\text{m}$ , obtained by Raman shifting in hydrogen of the  $1.06 \mu\text{m}$  radiation from a Q-switched Nd:YAG laser. The incident intensity was  $3 \frac{\text{MW}}{\text{cm}^2}$ , and the pulse length was about 20 ns. An apparent absorption coefficient of  $1 \times 10^{-2} \text{ cm}^{-1}$  was measured. The absorption was found to be intensity dependent, although it did not vary linearly with intensity, as would be expected if the cause were two-photon absorption. This excessively strong absorption is the result of the high intensities present when a Q-switched laser is used as the light source. This is

unfortunate because tunable near-infrared radiation is most readily obtained using pulsed sources. It is preferable to avoid the need to analyze intensity-dependent absorption data, since this adds one more degree of complication. The low intensity absorption limit could not be inferred from the data, except to say that it is less than  $10^{-2}\text{cm}^{-1}$ .

The second measurement was carried out at a wavelength of  $1.32\text{ }\mu\text{m}$ , obtained from a cw Nd:YAG laser. The absorption measured at this wavelength was  $1 \times 10^{-3}\text{cm}^{-1}$ . The source of this absorption is not known. However, three-phonon indirect band-to-band absorption has been reported to exist at these photon energies. The measurements that were carried out at  $1.32\text{ }\mu\text{m}$  are discussed in more detail in the attached paper, accepted for presentation at the OM85 conference sponsored by the National Bureau of Standards in Gaithersburg, MD in May, 1985.

Based on these data, some limited conclusions can be reached concerning the applicability of calorimetric spectroscopy, and closely related methods such as photoacoustic spectroscopy in the study of deep-level impurities in silicon. At wavelengths shorter than  $1.32\text{ }\mu\text{m}$ , the intrinsic background absorption can be expected to exceed  $1 \times 10^{-3}\text{cm}^{-1}$ . At longer wavelengths, the absorption should be lower over some wavelength interval, until a point is reached where free carrier absorption or lattice absorption will dominate. As a practical matter, it will be difficult to measure absorptions below  $10^{-3}\text{cm}^{-1}$  at cryogenic temperatures because of scattered light problems. Cold sample surfaces cryopump residual water vapor, resulting in frost that

strongly scatters incident light. In one study at Hughes, Malibu it was found that extreme cleaning measures were necessary at temperatures of 40K in order to reduce apparent background signals due to scattering below  $10^{-2}\text{cm}^{-1}$  [3]. In another study at the Air Force Weapons Laboratory, it was necessary to resort to ultrahigh vacuum technology in order to avoid surface cryopumping problems at liquid helium temperatures [4].

#### Summary

The principal limitations for the application of laser cryogenic calorimetric spectroscopy to the study of deep-level impurities in silicon are:

Scattered light

Free carrier absorption

Intensity-dependent absorption

Requirement for a single active deep-level transition

Requirement for heavily deep-doped samples

Availability of tunable cw near-infrared lasers.

#### References

1. References to laser calorimetry include the following:  
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3. Susan Allen, Ph.D., private communication
4. Alan Stewart, Ph.D., private communication



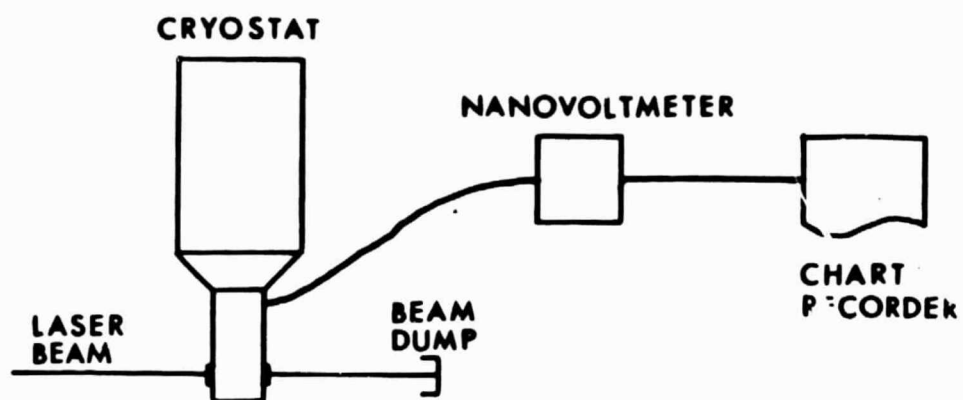


FIG. 1  
SYSTEM CONFIGURATION

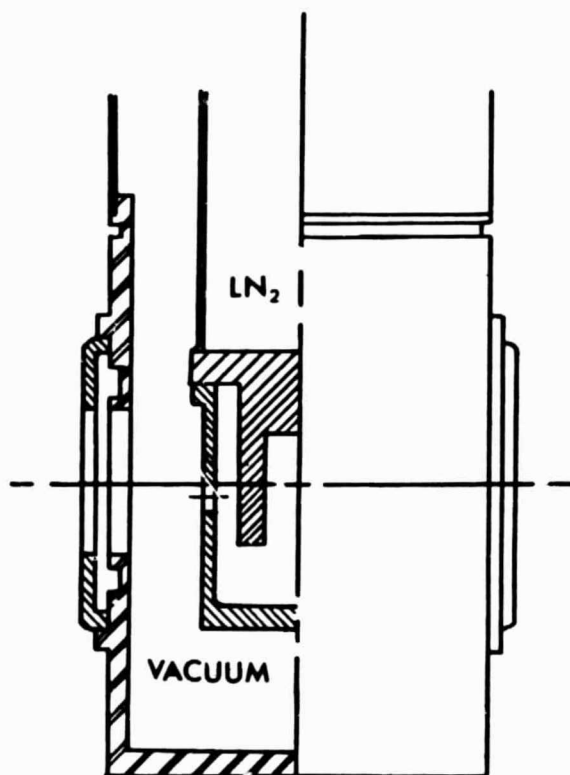


FIG. 2 CRYOSTAT  
DETAIL

FIG. 3 TYPICAL DATA

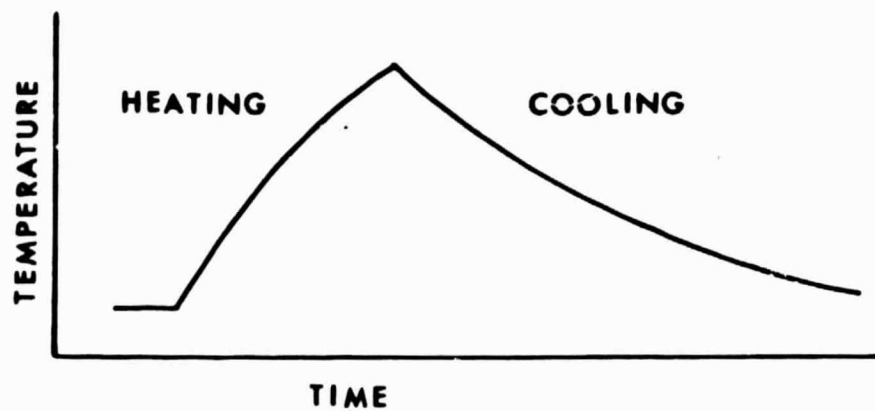


FIG. 4 PHOTO  
CROSS - SECTION

